

## Magnetization of Re-based double perovskites: Noninteger saturation magnetization disclosed

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Using static magnetic fields up to 30 T, the authors have measured the high-field magnetization in high-quality samples made from Re-based double perovskites:  $A_2\text{FeReO}_6$  ( $A_2=\text{Ca}_2, \text{Sr}_2, \text{BaSr}$ ) and  $\text{Sr}_2\text{CrReO}_6$ , with Curie temperatures ranging from 360 up to 610 K. The results indicate that the saturation magnetization in these compounds is higher than the assumed spin-only ionic values,  $3\mu_B/\text{f.u.}$  for  $A_2\text{FeReO}_6$  and  $1\mu_B/\text{f.u.}$  for  $\text{Sr}_2\text{CrReO}_6$ , which is explained by the large orbital contribution to the magnetization. Indirectly, these results show that Re-based double perovskites cannot be described as half-metals. © 2007 American Institute of Physics.

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Half-metals are magnetic materials with carriers showing only one spin direction at the Fermi level, either parallel or antiparallel to the magnetization direction, and have a huge potential in the field of spin electronics. Ferromagnetic double perovskites ( $A_2BB'O_6$ ,  $A$ =alkaline earth metals and  $B/B'$ =transition metals) have recently attracted great attention due to their presumed half-metallicity as well as high Curie temperature ( $T_C$ ). Thus,  $\text{Sr}_2\text{FeMoO}_6$  ( $T_C=420$  K),<sup>1</sup>  $\text{Ca}_2\text{FeReO}_6$  ( $T_C=520$  K),<sup>2</sup>  $\text{Sr}_2\text{CrReO}_6$  ( $T_C=610$  K),<sup>3</sup> and  $\text{Sr}_2\text{CrOsO}_6$  ( $T_C=720$  K) (Ref. 4) are currently being actively studied with this purpose. A review article on these exciting materials was recently published.<sup>5</sup>

The  $A_2\text{FeReO}_6$  ( $A_2=\text{Ca}_2, \text{Sr}_2, \text{Ba}_2$ ) compounds were already studied in the past,<sup>6</sup> way before the renewed interest in the light of applications for magnetoelectronics. In these compounds, it is generally assumed that five “localized”  $3d$  electrons produced by Fe ( $S=5/2$ ) will align antiparallely to two “delocalized” electrons shared by Fe and Re and mediating a double-exchange-like interaction through the oxygen orbitals. Ideally, the conduction electrons will show complete negative spin polarization at the Fermi level, say, half-metallicity. Such an ionic picture implies an expected spin-only saturation magnetization ( $M_S$ ) of  $3\mu_B/\text{f.u.}$  However, a number of striking features recently discovered in  $A_2\text{FeReO}_6$  have clearly demonstrated that the physics of these compounds is much more challenging than previously assumed. First, the ground state has been found to change from metallic for  $A_2=\text{Ba}_2$  to semiconducting for  $A_2=\text{Ca}_2$ ,<sup>2,7</sup> even though  $\text{Ca}_2\text{FeReO}_6$  shows the highest  $T_C$  in the series. An unexpected very large magnetic anisotropy was found and attributed to the intrinsic anisotropy of Re ions.<sup>8</sup> Strong magnetostructural effects have also been reported in this series by neutron diffraction,<sup>9</sup> which are also nicely reflected in a large anisotropic magnetostriction totally unexpected in ferromagnetic oxides without orbital instabilities.<sup>10</sup> The large spin-orbit coupling exhibited by the Re ions ( $5d$  element) in

this series has been disclosed through x-ray magnetic circular dichroism (XMCD) measurements that show the presence of a significant orbital moment.<sup>11</sup> With respect to the potentiality of these compounds for magnetoelectronic applications, the large intergrain magnetoresistance found in polycrystalline pellets suggested half-metallicity<sup>12</sup> even though this property has never been demonstrated. In this letter, we aim to disclose one of the standing controversies on Re-based double perovskites, i.e., the saturation magnetization of these materials and, indirectly, important aspects of their physical properties such as the existence or not of half-metallicity.

The compounds studied in the present work,  $A_2\text{FeReO}_6$  ( $A_2=\text{Ca}_2, \text{Sr}_2, \text{BaSr}$ ) and  $\text{Sr}_2\text{CrReO}_6$ , were “fresh” samples synthesized by solid-state reaction techniques, as described elsewhere.<sup>8,13</sup> The selected samples have a low amount of antisite (AS) disorder defects in order to make the conclusion robust (AS is known to decrease magnetization).<sup>14</sup> The amounts of AS are only 0.5% for  $\text{BaSrFeReO}_6$ , 2% for  $\text{Sr}_2\text{FeReO}_6$ , and 0% for  $\text{Ca}_2\text{FeReO}_6$ , which give us the opportunity to investigate  $M_S$  in almost-AS-free samples. We have carried out magnetization studies in the temperature range of 300–700 K by means of an ADE Electronics EV7 vibrating sample magnetometer with the sensitivity of  $10^{-6}$  emu. As previously reported,  $T_C$  for  $\text{BaSrFeReO}_6$ ,  $\text{Sr}_2\text{FeReO}_6$ , and  $\text{Ca}_2\text{FeReO}_6$  is found to be, respectively,  $\approx 360$ ,  $\approx 410$ , and  $\approx 520$  K.<sup>7,8</sup> Magnetization isotherms above  $T_C$  show the expected linear dependence with the magnetic field. From the extrapolation of the linear behavior onto the ordinate axis, the extrinsic magnetization caused by ferromagnetic impurities is estimated to be  $\approx 0.065$ ,  $\approx 0.25$ , and  $\approx 0.05$  emu/g for  $\text{BaSrFeReO}_6$ ,  $\text{Sr}_2\text{FeReO}_6$ , and  $\text{Ca}_2\text{FeReO}_6$ , respectively. This corresponds, respectively, to 0.2%, 0.7%, and 0.1% of the saturation magnetization values of  $\text{BaSrFeReO}_6$ ,  $\text{Sr}_2\text{FeReO}_6$ , and  $\text{Ca}_2\text{FeReO}_6$ , which allow us to discard any relevant influence on the reported effects.

Magnetization measurements up to 5 T have been performed with a Quantum Design superconducting quantum interference device (SQUID) magnetometer with sensitivity  $\approx 5 \times 10^{-7}$  emu. The magnetization values at 4 K under 5 T for  $\text{BaSrFeReO}_6$ ,  $\text{Sr}_2\text{FeReO}_6$ , and  $\text{Ca}_2\text{FeReO}_6$  are, respec-

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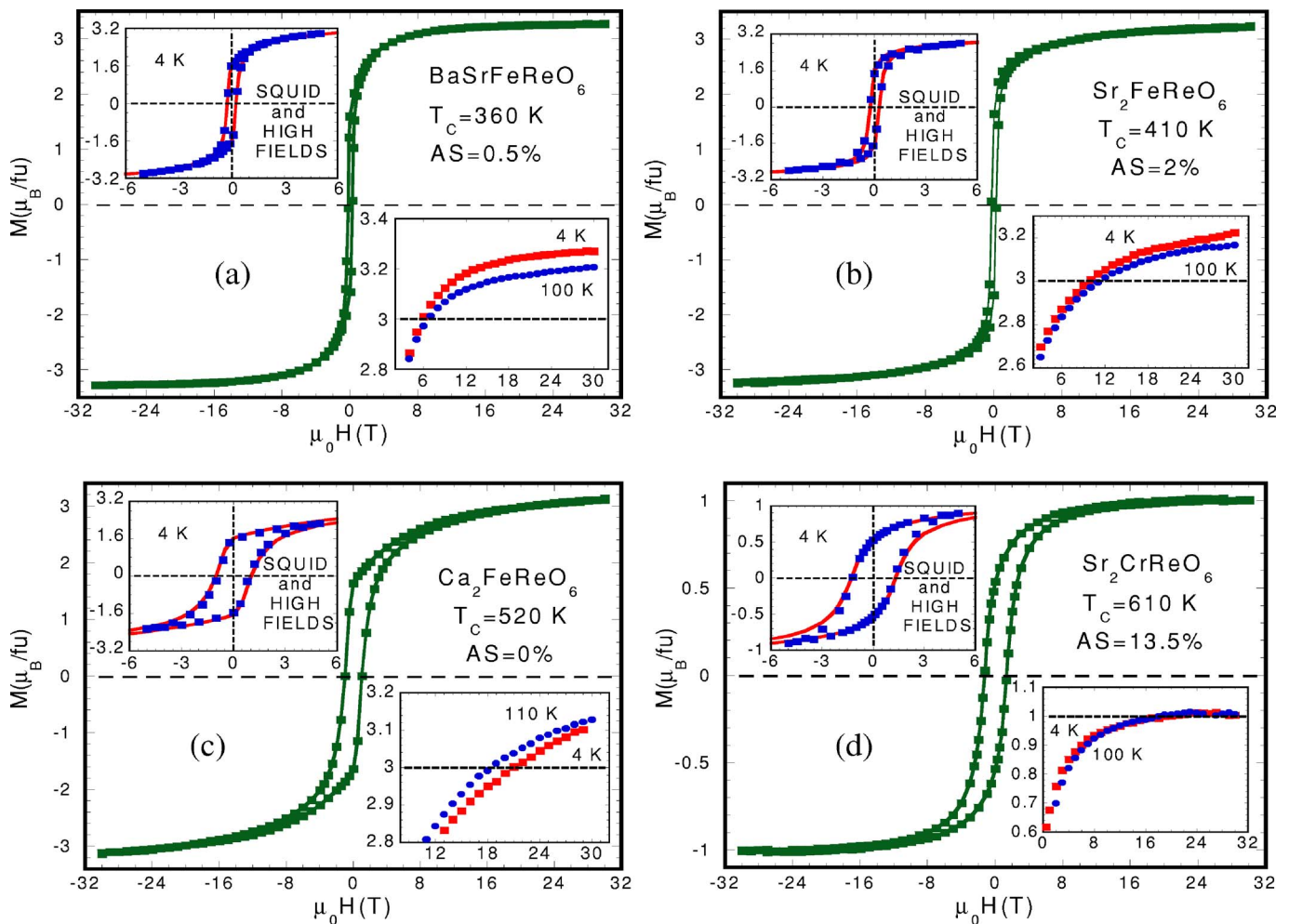


FIG. 1. (Color online) (a) Magnetization hysteresis loop at 4 K up to 30 T of BaSrFeReO<sub>6</sub>. Bottom inset: zoom in of the magnetization in the vicinity of 30 T. The line marks the value expected for the saturation magnetization without orbital contribution to the magnetization. Top inset: comparison between the magnetization results obtained with SQUID up to 5 T (squares) and the results obtained in the high-field installation (line). (b) The same for Sr<sub>2</sub>FeReO<sub>6</sub>. (c) The same for Ca<sub>2</sub>FeReO<sub>6</sub>. (d) The same for Sr<sub>2</sub>CrReO<sub>6</sub>.

tively, found to be  $2.98\mu_B/f.u.$ ,  $2.81\mu_B/f.u.$ , and  $2.25\mu_B/f.u.$ . Nevertheless, 5 T is not a sufficient field to saturate the magnetization. High-field magnetization measurements up to 30 T have been performed at the High Field Magnet Laboratory, Radboud University Nijmegen, Netherlands by using a Bitter coil. The magnetization is measured with the extraction method via two pick-up coils connected in series opposition. In Fig. 1(a) we show the magnetization hysteresis loop at 4 K up to 30 T of the BaSrFeReO<sub>6</sub> sample. Under the maximum field of 30 T the magnetization is found to be  $3.27\mu_B/f.u.$ , much above the previously assumed value of  $3\mu_B/f.u.$  As can be noticed in the inset of this figure, this compound is almost saturated under 30 T. This fact, together with the small value of AS (0.5%), allows us to establish the value of  $3.30(5)\mu_B/f.u.$  for the  $M_S$  of this compound if we use the expression  $M_S(\text{exp}) = M_S[(1-2)AS]$ , where  $M_S(\text{exp})$  is the measured experimental value and  $M_S$  is the value without AS. This dependence of the saturation magnetization on AS has been used in the past in double perovskites, with good agreement with the experimental results.<sup>14,15</sup> As shown in the inset of Fig. 1(a), the results obtained with the SQUID magnetometer up to 5 T superimpose in this field range to the measurements up to 30 T. The coercive field is around 0.24 T and the remanent magnetization is around 50% of the saturation value. As expected, the magnetization decreases as the temperature is increased. As shown in the inset of

Fig. 1(a), at 100 K and under the maximum field of 30 T the magnetization is found to be  $3.21\mu_B/f.u.$ , still much above  $3\mu_B/f.u.$  The slight increase of the magnetization between 100 and 4 K [see the inset of Fig. 1(a)] also allows us to discard any kind of spurious paramagnetic signal that could contribute to the measurement at 4 K. The measurements on Sr<sub>2</sub>FeReO<sub>6</sub> are shown in Fig. 1(b). Similar conclusions can be drawn for this compound. In this case, under the maximum field of 30 T the magnetization is found to be  $3.23\mu_B/f.u.$  at 4 K and  $3.17\mu_B/f.u.$  at 100 K. However, in this compound the tendency to saturate is less clear than for BaSrFeReO<sub>6</sub>, and it seems that a few more tesla are required to achieve saturation. Taking into account the level of antisites in this sample, one can estimate the  $M_S$  of this compound to be  $3.33(5)\mu_B/f.u.$  by using the expression introduced before. This is indeed only an approximate value due to the lack of complete magnetic saturation at 30 T. The lack of magnetic saturation under 30 T is evident in the Ca<sub>2</sub>FeReO<sub>6</sub> sample, whose results are shown in Fig. 1(c). Under the maximum field of 30 T the magnetization is found to be around  $3.12\mu_B/f.u.$  at 4 and 100 K. We ascribe the lack of increase of the  $M_S$  in the temperature range between 100 and 4 K to the fact that a structural transition between two monoclinic crystallographic structures takes place in this compound below 120 K.<sup>7,8</sup> The lack of magnetic saturation at 30 T in this compound prevents us from establishing an

accurate value for  $M_S$  even though we can state that it will be larger than the value obtained at 30 T,  $3.12\mu_B/f.u.$

These results demonstrate that these materials require very high fields to achieve magnetic saturation. The large coercive fields as well as saturation fields reflect a large magnetic anisotropy. It is remarkable that the coercive and saturation fields in these Re-based double perovskites are comparable to those observed in permanent magnets, suggesting a significant magnetocrystalline anisotropy that would be exciting to measure in single crystals or epitaxial films. Some recent theoretical articles have tried to tackle the physical properties of  $A_2FeRe(Mo)O_6$  with modern approaches. It was realized that the remarkable existence of a sizable magnetic moment on the nonmagnetic ion in Re (Mo) ferromagnetic double perovskites can be explained by the hopping interactions that produce the splitting of the spin-up and spin-down subbands of Re (Mo) and presumably give rise to half-metallicity at the Fermi level.<sup>1,5,12</sup> However, the physics of Re-based double perovskites is strikingly different from that of their Mo-based counterparts, and it was later argued that an important ingredient in the description of Re-based double perovskites is the significant spin-orbit coupling at Re ions producing a large Re orbital moment. Thus, calculations in  $Sr_2FeReO_6$  (Ref. 16) and  $Ba_2FeReO_6$  (Ref. 17) predicted values for the Re orbital moment which are comparable to experimental values found by XMCD measurements ( $\sim 0.3\mu_B/Re$  atom).<sup>11</sup> The Re orbital moment is antiparallel to the Re spin moment (as expected from less-than-half-filled  $5d$  orbitals) and parallel to the Fe spin moment. The significant Re orbital moment paves the way for a noninteger saturation magnetization, as we find experimentally, in sharp contrast to theories assuming only spin contribution to the magnetization.

Our results of noninteger saturation magnetization in  $A_2FeReO_6$  have a further important implication. Half-metallic double perovskites should satisfy the integer spin moment per f.u. criterion as a consequence of the integer number of total electrons (spin-up plus spin-down electrons) together with the gap at the Fermi level in the spin-up subband required to account for only spin-down electrons at the Fermi level.<sup>18</sup> A significant spin-orbit interaction will try to mix different spin states and, eventually, the spin-up subband gap at the Fermi level can disappear. From our finding of noninteger magnetization due to a strong spin-orbit coupling, it is tempting to put forward that  $A_2FeReO_6$  compounds do not realize the conditions required for half-metallicity. Theoretical support for this hypothesis has been reliably given by Vaitheeswaran *et al.*, who have calculated that the inclusion of the spin-orbit coupling in  $Ba_2FeReO_6$  will lead to the destruction of the half-metallic gap.<sup>17</sup> In the case of  $A_2FeMoO_6$  compounds, the Mo spin-orbit coupling is small and has no impact on the ground state. This is why in  $A_2FeMoO_6$  the saturation magnetization (originating exclusively from spin moments) is an integer value, and such compounds are presumably half-metals.<sup>5,18</sup>

For the sake of completeness, we include in this letter the results obtained during these experiments in another important Re-based double perovskite,  $Sr_2CrReO_6$ , with a high  $T_C$  (610 K). We have recently reported using pulsed magnetic fields that this compound requires around 20 T in order to saturate the magnetization.<sup>15</sup> In the current experiments we have used a  $Sr_2CrReO_6$  sample with a low antisite level (13.5%). The extrinsic magnetization caused by ferromag-

netic impurities is estimated to be  $\approx 0.009$  emu/g, which corresponds to only 0.1% of the saturation magnetization. As can be noticed in Fig. 1(d), we measure a  $M_S(\text{exp})$  of  $1.01\mu_B/f.u.$  at 4 K under 30 T, which is higher than the previously obtained value of  $0.95\mu_B/f.u.$ <sup>15</sup> By using the expression relating  $M_S$  and AS, we obtain  $M_S=1.38\mu_B/f.u.$  This value is close to the theoretical predictions in  $Sr_2CrReO_6$  by Vaitheeswaran *et al.*,<sup>19</sup> who predicted that the gap in the majority spin subband, and hence half-metallicity, is lost in this compound due to the strong spin-orbit coupling.

In summary we have found that  $M_S$  in  $A_2FeReO_6$  ( $A_2 = Ca_2, Sr_2, BaSr$ ) and  $Sr_2CrReO_6$  is much larger than the previously assumed spin-only ionic values, which can be explained in terms of a significant Re orbital moment that is antiparallel to the Re spin moment but parallel to the Fe magnetic moment.<sup>11</sup> The existence of noninteger saturation magnetization suggests that Re-based double perovskites are not half-metals, as previously assumed. Nevertheless, for  $Sr_2CrReO_6$  it has been calculated that the carriers at the Fermi level remain highly polarized ( $>90\%$ ) (Ref. 19) and could still be very attractive for applications in spin electronics.

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